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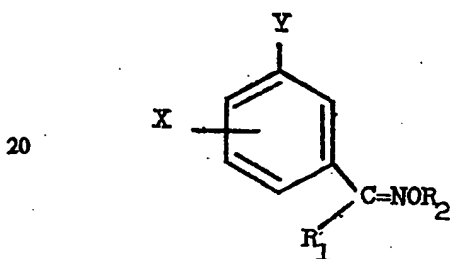
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(54) PHENYL KETOXIME DERIVATIVES

(71) We, SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V., formerly Shell Internationale Research Maatschappij N.V., a company organised under the laws of The Netherlands, of 30 Carel van Bylandtlaan, The Hague, The Netherlands, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to novel phenyl ketoxime derivatives which exhibit herbicidal and fungicidal properties, to processes for their preparation and to compositions containing them.

Accordingly the present invention provides phenyl ketoxime derivatives of general formula:—



25 wherein R₁ represents an alkyl group; R₂ represents a hydrogen atom, an alkyl or aralkyl group, a phenyl group substituted by nitro and by fluoroalkyl, or an acyl group; X represents a hydrogen or halogen atom, or an alkoxy, alkylthio or alkylureido group; and Y represents an amino, ureido or thioureido group optionally substituted by alkyl, phenyl, alkylphenyl or by acyl.

The term "acyl" is used herein in its broadest sense and denotes an organic radical formed by the removal of a hydroxyl group from an organic acid. The term, therefore, includes not only groups derived from carboxylic acids, for example alkanoyl or carbamoyl, but also groups derived from substituted carbonic acids, for example alkoxy-carbonyl or aralkoxy-carbonyl.

Preferred phenyl ketoxime derivatives are those wherein R₁ represents an alkyl group of 1—6 carbon atoms, for example methyl or propyl; R₂ represents a hydrogen atom, an alkyl group of 1—6 carbon atoms, for example methyl, a benzyl group, a phenyl group substituted by one or two nitro groups and by a fluoroalkyl group of 1—6 carbon atoms, for example by trifluoromethyl, an optionally chloro-substituted alkanoyl group of up to 10 carbon atoms, for example acetyl, trichloroacetyl or octanoyl, an alkanoyl group of up to 6 carbon atoms substituted by a phenoxy group bearing chloro or alkyl substituents, for example dichlorophenoxyacetyl, trichlorophenoxyacetyl, or chloro-methylphenoxyacetyl, an alkenoyl group of up to 12 carbon atoms, for example undecanoyl, a benzyloxy-carbonyl group, a chloro-substituted benzoyl group for example trichlorobenzoyl, or a carbamoyl group mono- or di-N-substituted by alkyl of 1—6 carbon atoms, for example by methyl; X represents a hydrogen or chlorine atom, or an alkoxy, alkylthio, or alkylureido group in which the alkyl group is of 1—6 carbon atoms, for example methoxy, methylthio or methylureido; and Y represents an amino group substituted by alkyl of 1—6 carbon atoms, for example by methyl, by alkanoyl of up to 6 carbon atoms optionally bearing a chloro or chloro-phenoxy substituent, for example by acetyl, chloroacetyl, propionyl or by dichlorophenoxyacetyl,

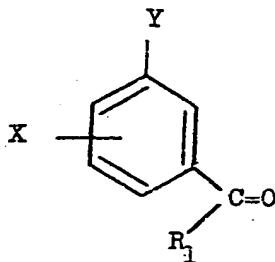
by alkoxycarbonyl of up to 6 carbon atoms, for example by ethoxycarbonyl or by isopropoxycarbonyl, or by benzyloxycarbonyl, a ureido group optionally substituted by one or two alkyl groups of 1-6 carbon atoms, for example by methyl, or by a phenyl or tolyl group, or a thioureido group substituted by alkanoyl of up to 6 carbon atoms, for example by acetyl.

The following phenyl ketoxime derivatives are particularly preferred:—

3'-(N'-methylureido)acetophenone oxime,
3'-(N',N'-dimethylureido) acetophenone O-methyl oxime and

3'-(N'-methylureido) acetophenone O-(4-chloro-2-methylphenoxyacetyl) oxime.

The invention includes also a process for preparing the phenyl ketoxime derivatives of formula I wherein R_2 represents a hydrogen atom or an alkyl group, which comprises reacting a phenyl ketone of general formula:—



II

with a hydroxylamine derivative of formula:—



III

The hydroxylamine derivative is conveniently used in the form of an acid salt such as the hydrochloride and, in this case, the reaction is suitably carried out in the presence of a base which may, for example, be an alkali metal hydroxide such as sodium hydroxide, an alkali metal salt of a weak organic acid such as sodium acetate, or a tertiary amine such as pyridine. The reaction is preferably carried out in an aqueous alcoholic solvent, for example aqueous ethanol or aqueous isopropanol.

The phenyl ketoxime derivative of formula I wherein R_2 represents an aralkyl or acyl group or a phenyl group substituted by nitro and by fluoroalkyl, are prepared by reacting the corresponding compound wherein R_2 represents a hydrogen atom with a base, for example an alkali metal hydride such as sodium hydride, or a tertiary amine such as triethylamine or pyridine, and a halo compound of formula:—



IV

wherein Hal represents a halogen, suitably

chlorine, atom. The reaction is preferably carried out in an organic solvent such as ether or benzene.

Those compounds wherein R_2 represents a mono-N-alkyl-substituted carbamoyl group may alternatively be obtained by reacting the corresponding compound of formula I wherein R_2 represents a hydrogen atom with an alkyl isocyanate, suitably in the presence of a tertiary amine such as triethylamine and in an organic solvent such as methylene chloride.

As mentioned above the phenyl ketoxime derivative of the invention are of interest as herbicides and fungicides and the invention therefore includes pesticidal compositions comprising a carrier or a surface-active agent, or both a carrier and a surface-active agent, together with, as active ingredient, at least one phenyl ketoxime derivative of the invention. Likewise the invention includes also a method of combating unwanted plant growth and/or fungi at a locus which comprises applying to the locus a phenyl ketoxime derivative or composition of the invention. The herbicidal activity of the compounds is particularly marked against broad-leaved weeds while fungicidal activity is exhibited particularly against fungal diseases of cereal crops such as wheat.

The term 'carrier' as used herein means a solid or fluid material, which may be inorganic or organic and of synthetic or natural origin, with which the active compound is mixed or formulated to facilitate its application to the plant, seed, soil or other object to be treated, or its storage, transport or handling.

The surface-active agent may be an emulsifying agent or a dispersing agent or a wetting agent; it may be nonionic or ionic. Any of the carrier materials or surface-active agents usually applied in formulating pesticides may be used in the compositions of the invention and suitable examples of these are to be found, for example, in our specification No. 1,232,930.

The compositions of the invention may be formulated as wettable powders, dusts, granules, solutions, emulsifiable concentrates, emulsions, suspension concentrates and aerosols. Wettable powders are usually compounded to contain 25, 50 or 75% w of toxicant and usually contain, in addition to solid carrier, 3-10% w of a dispersing agent and, where necessary, 0-10% w of stabiliser(s) and/or other additives such as penetrants or stickers. Dusts are usually formulated as a dust concentrate having a similar composition to that of a wettable powder but without a dispersant, and are diluted in the field with further solid carrier to give a composition usually containing 4-10% w of toxicant. Granules are usually prepared to have a size between 10 and 100 BS mesh (1.676-0.152mm), and may be manufactured by agglomeration or impregnation techniques. Generally granules will contain 1-25% w toxicant and 0-10% w of

additives such as stabilisers, slow release modifiers and binding agents. Emulsifiable concentrates usually contain, in addition to the solvent and, when necessary, co-solvent, 10—50% w/v toxicant, 2—20% w/v emulsifiers and 0—20% w/v of appropriate additives such as stabilisers, penetrants and corrosion inhibitors. Suspension concentrates are compounded so as to obtain a stable, non-sedimenting, flowable product and usually contain 10—75% w toxicant, 0.5—15% w of dispersing agents, 0.1—10% of suspending agents such as protective colloids and thixotropic agents, 0—10% w of appropriate additives such as defoamers, corrosion inhibitors, stabilisers, penetrants and stickers, and as carrier, water or an organic liquid in which the toxicant is substantially insoluble; certain organic solids or inorganic salts may be dissolved in the carrier to assist in preventing sedimentation or as antifreeze agents for water.

Aqueous dispersion and emulsions, for example, compositions obtained by diluting a wettable powder or a concentrate according to the invention with water, also lie within the scope of the present invention. The said emulsions may be of the water-in-oil or of the oil-

in-water type, and may have a thick 'mayonnaise'-like consistency.

The compositions of the invention may also contain other ingredients, for example other compounds possessing pesticidal, particularly insecticidal, acaricidal, herbicidal or fungicidal, properties.

The invention is illustrated further in the following examples.

Example 1

3'-Ethoxycarbonylaminoacetophenone oxime 3'-Ethoxycarbonylaminoacetophenone (5.0 g) was added to a solution of hydroxylamine hydrochloride (3.5 g) and pyridine (3.8 ml) in ethanol (50 ml) and the mixture was heated under reflux for 4 hours. The reaction mixture was then evaporated to dryness, water (50 ml) was added to the residue and the aqueous mixture was extracted with ethyl acetate (50 ml). The organic extract was washed in turn with 2N hydrochloric acid, sodium bicarbonate and water and then dried. The solvent was then removed under reduced pressure and the solid residue recrystallised from ethyl acetate to give the desired product having a m.p. 123—125°C.

Analysis

Calculated for $C_{11}H_{14}N_2O_3$: C 59.6; H 6.4; N 12.6%
Found : C 59.8; H 6.4; N 12.4%

Example 2

3-Ethoxycarbonylamino-phenyl propyl ketoxime

3-Ethoxycarbonylamino-phenyl propyl ketone (9.4 g), sodium acetate (3.3 g), hydroxylamine hydrochloride (2.8 g) and water (20 ml) in iso-

propanol (100 ml) were heated together under reflux for 3 hours. The mixture was then poured into water and the white precipitate formed was filtered off to give the desired product having a m.p. 142—143°C.

Analysis

Calculated for $C_{12}H_{16}N_2O_3$: C 62.4; H 7.2; N 11.2%
Found : C 62.2; H 7.3; N 11.1%

Example 3

3'-Propionamidoacetophenone O-methyl-oxime

3'-Propionamidoacetophenone (4.8 g) was dissolved in ethanol (50 ml) and to this solution was added a solution containing sodium hydroxide (1.0 g) and methoxyamine hydrochloride (2.3 g) in water (50 ml). The mixture

was heated under reflux for 5 hours. The ethyl alcohol was then removed under reduced pressure and the aqueous mixture was extracted with ethyl acetate (2 × 5 ml). The organic extracts were dried and evaporated to dryness to yield the desired product having a m.p. 105—106°C.

Analysis

Calculated for $C_{12}H_{16}N_2O_2$: C 65.5; H 7.3; N 12.7%
Found : C 65.4; H 7.5; N 12.7%

4.

Example 4

3'-Ethoxycarbonylaminoacetophenone
O-(N',N'-dimethylcarbamoyl)oxime

- 5 Sodium hydride (0.24 g, as 50% dispersion in oil) was added to 3'-ethoxycarbonylaminoacetophenone oxime (1.1 g) in ether (50 ml) and the mixture stirred for 15 minutes. Dimethylcarbamoyl chloride (0.5 ml) in ether

(10 ml) was then added to the mixture which was then heated under reflux for one hour. 10 The mixture was poured into water and the ether layer was separated, dried and evaporated to dryness. The residue was recrystallised from a mixture of ether and petroleum ether (b.p. 60—80°C) to give the desired product 15 having a mp 162—164°C.

Analysis

Calculated for $C_{11}H_{11}N_3O_3$: C 57.3; H 6.5; N 14.3%
Found: C 57.6; H 6.7; N 14.3%

Example 5

3'-Ethoxycarbonylaminoacetophenone
O-(N'-methylcarbamoyl)oxime

- 20 3'-Ethoxycarbonylaminoacetophenone oxime (4.2 g), methyl isocyanate (1.4 ml) and triethyl-

amine in methylene chloride (40 ml) were 25 heated together under reflux for 2 hours. The residue after removal of the solvent was recrystallised from benzene to yield the desired product having a m.p. 101—103°C.

Analysis

Calculated for $C_{11}H_{11}N_3O_3$: C 55.9; H 6.1; N 15.1%
Found: C 56.2; H 6.2; N 15.1%

Example 6

3'-(N',N'-Dimethylureido)acetophenone
O-(4-chloro-2-methylphenoxyacetyl)oxime

- 35 3'-(N',N'-Dimethylureido)acetophenone oxime (1.1g, prepared by a similar method to that of example 3) and triethylamine (0.5g) in acetone (50 ml) were cooled to below 5°C. 4-Chloro-2-methylphenoxyacetyl chloride (1.1g) 40 in acetone (20 ml) was added to the cooled

solution over a period of 10 minutes and the mixture was stirred at 20°C for a further 3 hours. Ether (100 ml) was then added to the reaction mixture which was then filtered. 45 The filtrate was evaporated to dryness and the residue was recrystallised from ether (20 ml) to give the desired product having a m.p. 143—145°C.

Analysis

Calculated for $C_{20}H_{22}N_3O_4Cl$: C 59.5; H 5.4; N 10.4%
Found: C 59.1; H 5.8; N 10.3%

Example 7

- 55 Following procedures similar to those Examples 1—3 further compounds were pre-

pared, whose physical characteristics and analyses are set out in Table 1.

TABLE I

Compound	Melting Point °C	Analysis
3'-isopropoxycarbonylaminoacetophenone oxime	121 — 123	Calculated for $C_{12}H_{16}N_2O_3$ Found : C 61.0; H 6.8; N 11.9% : C 60.6; H 6.8; N 11.6%
3'-propionamidoacetophenone oxime	135 — 136	Calculated for $C_{11}H_{14}N_2NO_2$ Found : C 64.1; H 6.8; N 13.6% : C 63.9; H 7.0; N 13.5%
3'-benzyloxycarbonylaminoacetophenone oxime	170 — 172	Calculated for $C_{14}H_{16}N_2O_3$ Found : C 67.6; H 5.7; N 9.8% : C 67.6; H 5.8; N 9.8%
3'-acetamidoacetophenone oxime	194 — 196	Calculated for $C_{10}H_{12}N_2O_3$ Found : C 62.5; H 6.3; N 14.6% : C 62.7; H 6.4; N 14.6%
3'-(chloroacetamido)acetophenone oxime	150 — 152	Calculated for $C_{10}H_{11}N_2O_3Cl$ Found : C 53.0; H 4.9; N 12.3; Cl 15.7% : C 52.6; H 5.2; N 12.1; Cl 15.6%
3'-benzyloxycarbonylaminoacetophenone O-methylloxime	51 — 53	Calculated for $C_{17}H_{18}N_2O_3$ Found : C 68.4; H 6.1; N 9.4% : C 68.2; H 6.3; N 9.5%
3'-(N',N'-dimethylureido)acetophenone oxime	187 — 188	Calculated for $C_{11}H_{15}N_3O_3$ Found : C 59.7; H 6.8; N 19.0% : C 59.2; H 6.5; N 19.0%
3'-(N',N'-dimethylureido)acetophenone O-methylloxime	168 — 170	Calculated for $C_{12}H_{17}N_3O_3$ Found : C 61.3; H 7.2; N 17.9% : C 61.6; H 7.1; N 17.8%
3'-(N'-methylureido)acetophenone oxime	175 — 177	Calculated for $C_{10}H_{13}N_2O_3$ Found : C 57.9; H 6.3; N 20.3% : C 57.4; H 6.3; N 20.2%
3'-(N'-methylureido)acetophenone O-methyl-oxime	134 — 135	Calculated for $C_{11}H_{15}N_3O_3$ Found : C 59.7; H 6.8; N 18.9% : C 59.0; H 6.7; N 18.6%
3'-(N',N'-dimethylureido)acetophenone O-octanoyloxime	Oil	Calculated for $C_{10}H_{23}N_3O_3$ Found : C 65.7; H 8.4; N 12.1% : C 66.0; H 8.8; N 11.8%

TABLE 1 (Continued)

Compound	Melting Point °C	Analysis
3'-(N',N'-dimethylureido)acetophenone O-acetylloxime	126 — 129	Calculated for $C_{13}H_{17}N_3O_3$ Found : C 59.3; H 6.5; N 16.0% : C 59.7; H 6.7; N 15.9%
3'-(N'-methylureido)acetophenone O-acetylloxime	135 — 138	Calculated for $C_{12}H_{16}N_3O_3$ Found : C 58.3; H 5.3; N 17.0% : C 57.9; H 5.1; N 16.6%
3'-(N'-methylureido)acetophenone O-octanoyloxime	100 — 102	Calculated for $C_{19}H_{27}N_3O_3$ Found : C 64.8; H 8.2; N 12.6% : C 64.4; H 8.1; N 12.7%
3'-ureidoacetophenone oxime	235 — 237	Calculated for $C_9H_{11}N_3O_2$ Found : C 56.0; H 5.7; N 21.8% : C 56.1; H 5.9; N 22.1%
2'-chloro-5'-(N'-methylureido)acetophenone oxime	142 — 144	Calculated for $C_{10}H_{12}N_3O_2Cl$ Found : C 47.9; H 5.2; N 16.8% : C 48.1; H 5.1; N 16.6%
3'-(N',N'-dimethylureido)acetophenone O-(benzyloxycarbonyl)oxime	165 — 167	Calculated $C_{19}H_{21}N_3O_4$ Found : C 64.2; H 6.0; N 11.8% : C 63.8; H 6.2; N 12.2%
3'-(N'-methylureido)acetophenone O-4-(chloro-2-methyl phenoxyacetyl)oxime	128 — 130	Calculated for $C_{19}H_{20}N_3O_4Cl$ Found : C 58.5; H 5.1; N 10.8; Cl 9.1% : C 58.8; H 5.2; N 10.6; Cl 9.5%
3'-(N'-methylureido)acetophenone O-benzyl-oxycarbonyl)oxime	112 — 114	Calculated for $C_{18}H_{19}N_3O_4$ Found : C 63.3; H 5.6; N 12.3% : C 63.1; H 5.7; N 12.4%
3'-(N'-methylureido)acetophenone O-tri-chloroacetyl)oxime	151 — 153	Calculated for $C_{12}H_{12}N_3O_3Cl_3$ Found : C 40.9; H 3.4; N 11.9% : C 41.0; H 3.5; N 11.9%
3'-(N',N'-dimethylureido)acetophenone O-(2,4-dichloro phenoxyacetyl)oxime	178 — 180	Calculated for $C_{19}H_{16}N_3O_4Cl_2$ Found : C 53.8; H 4.5; N 9.9% : C 53.7; H 4.6; N 9.8%

TABLE 1 (Continued)

Compound	Melting Point °C	Analysis
3'-(N',N'-dimethylureido)acetophenone O-(2,4,5-trichlorophenoxy)oxime	181 — 183	Calculated for $C_{19}H_{18}N_3O_4Cl_3$ Found : C 49.7; H 3.9; N 9.2% : C 50.0; H 4.2; N 8.9%
3'-(N'-methylureido)acetophenone O-(10-undecenoyl)oxime	64 — 66	Calculated for $C_{21}H_{21}N_2O_3$ Found : C 67.5; H 8.4; N 11.3% : C 67.7; H 8.5; N 10.9%
3'-(N'-acetylthioureido)acetophenone oxime	169 — 171	Calculated for $C_{11}H_{13}N_2SO_2$ Found : C 52.5; H 5.2; N 16.7; S 12.8% : C 51.1; H 5.2; N 16.4; S 12.8%
3'-(N-(2,4-dichlorophenoxyacetyl)amino)-acetophenone oxime	188 — 190	Calculated for $C_{18}H_{14}N_2O_3Cl_2$ Found : C 54.4; H 4.0; N 7.9% : C 54.1; H 3.9; N 8.3%
3'-(N',N'-dimethylureido)acetophenone oxime	157 — 159	Calculated for $C_{11}H_{13}N_2O_2$ Found : C 59.7; H 6.8; N 18.9% : C 59.7; H 6.9; N 18.6%
3'-(N-methylamino)acetophenone oxime	Oil	Calculated for $C_9H_{12}N_2O$ Found : C 65.8; H 7.4; N 17.1% : C 65.5; H 7.4; N 17.3%
3'-(N-(2,4-dichlorophenoxyacetyl)amino)-acetophenone O-(N'-methylcarbamoyl)oxime	147 — 150	Calculated for $C_{18}H_{17}N_3O_4Cl_2$ Found : C 52.7; H 4.2; N 10.3% : C 52.7; H 4.4; N 10.3%
3'-(N'-methylureido)acetophenone O-(N'-methylcarbamoyl)oxime	165 — 167	Calculated for $C_{13}H_{14}N_2O_3$ Found : C 54.5; H 6.1; N 21.2% : C 54.2; H 6.1; N 21.2%
3'-(N'-methylureido)acetophenone O-(2,4-dichlorophenoxyacetyl) oxime	160 — 162	Calculated for $C_{18}H_{17}N_3O_4Cl_2$ Found : C 52.7; H 4.2; N 10.3% : C 52.3; H 4.3; N 10.1%
3'-(N'-methylureido)acetophenone O-(2,4,5-trichlorophenoxyacetyl) oxime	191 — 193	Calculated for $C_{18}H_{13}N_3O_4Cl_3$ Found : C 48.7; H 3.6; N 9.4% : C 48.4; H 3.7; N 9.4%

TABLE 1 (Continued)

Compound	Melting Point, °C	Analysis
3'-(N'-methylureido)acetophenone O-(2,4,5-trichlorobenzoyl)oxime	182 — 184	Calculated for $C_{17}H_{14}N_3O_3Cl_3$: C 49.2; H 3.4; N 10.1% Found : C 49.0; H 3.6; N 10.0%
3'-(N'-methylureido)acetophenone O-(2-nitro-4-trifluoromethyl phenyl)oxime	140 — 142	Calculated for $C_{17}H_{13}N_4O_4F_3$: C 51.5; H 3.8; N 14.0% Found : C 51.8; H 4.0; N 13.8%
3'-(N'-methylureido)acetophenone O-benzoyloxime	155 — 157	Calculated for $C_{17}H_{13}N_3O_3$: C 68.7; H 6.4; N 14.0% Found : C 68.3; H 6.3; N 13.8%
5'-(N'-methylureido)-2'-methoxyacetophenone oxime	203 — 205	Calculated for $C_{17}H_{15}N_3O_3$: C 55.7; H 6.3; N 17.2% Found : C 55.3; H 6.0; N 17.4%
3'-(N'-phenylureido)acetophenone oxime	197 — 199	Calculated for $C_{15}H_{11}N_3O_2$: C 66.9; H 5.6; N 15.6% Found : C 67.0; H 5.5; N 15.6%
3'-(N'- <i>m</i> -tolylureido)acetophenone oxime	184 — 186	Calculated for $C_{16}H_{13}N_3O_2$: C 67.8; H 6.1; N 14.8% Found : C 68.6; H 6.3; N 14.3%
3'-(N'-methylureido)acetophenone O-(2,6-dinitro-4-trifluoromethylphenyl)oxime	149 — 151	Calculated for $C_{17}H_{14}N_4O_6F_3$: C 46.2; H 3.2; N 15.9% Found : C 46.8; H 3.5; N 15.6%
3',5'-bis(N'-methylureido)acetophenone oxime (as hemi-hydrate)	220 — 222	Calculated for $C_{17}H_{17}N_3O_3 \cdot \frac{1}{2}H_2O$: C 50.1; H 6.2; N 24.3% Found : C 50.5; H 5.9; N 24.0%
2'-methylthio-5'-(N'-methylureido)acetophenone oxime	167 (dec)	Calculated for $C_{11}H_{13}N_3SO_2$: C 52.2; H 5.9; N 16.6% Found : C 52.6; H 6.2; N 16.4%

Example 8 Herbicidal Activity

To evaluate their herbicidal activity, the compounds of the invention were tested using as a representative range of plants:—maize, *Zea mays* (Mz); rice, *Oryza sativa* (R); barnyard grass, *Echinochloa crusgalli* (BG); pea, *Pisum sativum* (P); linseed, *Linum usitatissimum* (L); mustard, *Sinapis alba* (M); and sugar beet, *Beta vulgaris* (SB).

The tests fall into two categories, pre-emergence and post-emergence. The pre-emergence tests involved spraying a liquid formulation of the compound onto the soil in which the seeds of the plant species mentioned above had recently been sown. The post-emergence tests involved two types of test, viz. soil drench and foliar spray tests. In the soil drench tests the soil in which seedling plants of the above species were growing, was drenched with a liquid formulation containing a compound of the invention, and in the foliar spray tests the seedling plants were sprayed with such a formulation.

The soil used in the tests was a steam-sterilised, modified John Innes Compost mixture in which half the peat, by loose bulk, had been replaced by vermiculite.

The formulations used in the tests were prepared by diluting with water and solutions of the compounds in acetone containing 0.4% by weight of an alkylphenol/ethylene oxide condensate available under the trade name

Triton (registered Trade Mark) X—155. In the soil spray and foliar spray tests the acetone solutions were diluted with an equal volume of water and the resulting formulations applied at two dosage levels corresponding to 10 and 1 kilograms of active material per hectare respectively in a volume equivalent to 400 litres per hectare. In the soil drench tests one volume of the acetone solution was diluted to 155 volumes with water and the resulting formulation applied at one dosage level equivalent to 10 kilograms of active material per hectare in a volume equivalent to approximately 3,000 litres per hectare.

In the pre-emergence tests untreated sown soil and in the post-emergence tests untreated soil bearing seedling plants were used as controls.

The herbicidal effects of the compounds were assessed visually seven days after spraying the foliage and drenching the soil and eleven days after spraying the soil, and were recorded on a 0—9 scale. A rating 0 indicates no effect on the treated plants, a rating 2 indicates a reduction in fresh weight of stem and leaf of the plants of approximately 25%, a rating 5 indicates a reduction of approximately 55%, a rating 9 indicates a reduction of 95% etc.

The results of the tests are set out in Table 2.

TABLE 2

Compound	Dosage kg/ha	Post-Emergence (Plants)												Pre-Emergence (Seeds)								
		Soil Drench						Foliar Spray						Soil Spray								
		Mz	R	BG	P	L	M	SB	Mz	R	BG	P	L	M	SB	Mz	R	BG	P	L	M	SB
3'-ethoxycarbonylaminoacetophenone oxime	10 1	1	1	8	0	9	9	9	5	7	9	2	9	9	9	1	5	8	0	8	9	9
3'-isopropoxycarbonylaminoacetophenone oxime	10 1	0	1	8	0	9	9	9	0	0	7	0	8	9	9	0	4	7	0	9	9	9
3'-propionamidoacetophenone oxime	10 1	0	6	7	3	9	9	9	3	8	8	6	9	9	9	0	0	3	0	0	7	7
3'-ethoxycarbonylaminoethyl propyl ketoxime	10 1	0	0	3	0	7	9	9	0	0	6	0	9	9	9	0	0	0	0	0	7	9
3'-benzyloxycarbonylaminoacetophenone oxime	10 1	0	0	0	0	0	0	0	0	0	0	1	6	9	9	1	2	1	0	0	7	2
3'-acetamidoacetophenone oxime	10 1	0	0	2	1	3	1	2	0	1	5	3	9	9	7	0	0	0	0	0	4	0
3'-propionamidoacetophenone O-methyloxime	10 1	1	0	0	2	5	9	7	4	5	4	7	8	9	9	0	0	0	0	3	8	6
3'-(chloroacetamido)acetophenone oxime	10 1	0	0	0	0	0	0	0	0	0	2	2	3	8	8	0	0	0	0	0	0	0

TABLE 2 (Continued)

Compound	Dosage kg/ha	Post-Emergence (Plants)												Pre-Emergence (Seeds)											
		Soil Drench						Foliar Spray						Soil Spray											
		Mz	R	B	G	P	L	M	SB	Mz	R	B	G	P	L	M	SB	Mz	R	B	G	P	L	M	SB
3'-benzyloxy carbonyl amino acetophenone O-methyl oxime	10 1	0	0	0	0	0	1	0		1	1	3	2	7	9	9		0	0	2	0	1	8	9	
3'-(N,N'-dimethylureido)acetophenone oxime	10 1	5	8	9	7	9	9	9		5	8	9	3	9	9	9		4	1	9	1	9	9	9	
3'-(N,N'-dimethylureido)acetophenone O-methyl oxime	10 1	3	5	2	6	9	9	9		0	3	3	5	8	9	9		4	1	9	2	8	9	9	
3'-(N'-methylureido)acetophenone oxime	10 1	1	3	8	3	9	9	9		4	6	9	6	9	9	9		4	3	9	1	9	9	9	
3'-(N'-methylureido)acetophenone O-methyl oxime	10 1	0	5	5	2	7	9	8		0	2	9	3	9	9	9		4	3	8	0	6	9	9	
3'-(N,N'-dimethylureido)acetophenone O-octanoyloxime	10 1	-	-	-	-	-	-	-		-	2	9	-	8	9	-		-	1	6	-	6	8	-	
3'-(N,N'-dimethylureido)acetophenone O-(4-chloro-2-methylphenoxyacetyl)oxime	10 1	-	-	-	-	-	-	-		7	8	9	7	9	9	9		7	9	9	9	9	9	9	

TABLE 2 (Continued)

Compound	Dosage kg/ha	Post-Emergence (Plants)												Pre-Emergence (Seeds)											
		Soil Drench						Foliar Spray						Soil Spray											
		Mz	R	BG	P	L	M	SB	Mz	R	BG	P	L	M	SB	Mz	R	BG	P	L	M	SB			
3'-(N',N'-dimethylureido)aceto-phenone O-acetyloxime	10 1	6	6	9	4	9	9	9	2	8	9	8	9	9	9	6	4	9	4	9	9	9			
3'-(N'-methylureido)aceto-phenone O-acetyloxime	10 1	-	-	-	-	-	-	-	8	9	9	7	9	9	9	7	6	9	2	9	9	9			
3'-(N'-methylureido)aceto-phenone O-octanoyloxime	10 1	6	9	9	7	9	9	9	7	9	9	4	9	9	9	5	6	9	0	8	9	9			
3'-ureidoacetophenone oxime	10 1	0	0	3	0	0	0	0	0	0	4	3	6	8	7	0	4	3	0	0	5	4			
2'-chloro-5'-(N'-methylureido)-acetophenone oxime	10 1	0	4	6	0	3	7	8	0	2	7	1	7	8	7	1	1	8	0	5	9	9			
3'-(N',N'-dimethylureido)aceto-phenone O-benzoyloxycarbonyl)-oxime	10 1	7	9	9	7	9	9	9	2	7	9	5	9	9	9	5	5	9	0	7	8	9			
3'-(N'-methylureido)acetophenone O-(4-chloro-2-methylphenoxy-acetyl)oxime	10 1	5	5	8	7	9	9	9	6	7	9	8	9	9	9	8	9	9	9	9	9	9			

TABLE 2 (Continued)

Compound	Dosage kg/ha	Post-Emergence (Plants)												Pre-Emergence (Seeds)											
		Soil Drench						Foliar Spray						Soil Spray											
		Mz	R	B	G	P	L	M	SB	Mz	R	B	G	P	L	M	SB	Mz	R	B	G	P	L	M	SB
3'-(N'-methylureido)acetophenone O-(benzyloxycarbonyl)oxime	10 1	6	9	9	3	9	9	9	9	2	6	9	3	9	9	9	9	2	3	9	0	7	9	9	9
3'-(N'-methylureido)acetophenone O-(2,4-dichlorophenoxy acetyl)oxime	10 1	4	4	8	7	9	9	9	9	4	7	9	8	9	9	9	9	8	9	9	9	9	9	9	9
3'-(N'-methylureido)acetophenone O-(2,4,5-trichlorophenoxyacetyl) oxime	10 1	0	0	0	0	1	0	1	1	3	7	9	9	9	9	9	8	5	8	8	7	9	9	9	9
3'-(N'-methylureido)acetophenone O-(2,4,5-trichlorobenzoyl)oxime	10 1	0	0	0	3	1	1	1	5	5	8	8	8	9	9	9	9	8	9	9	9	9	9	9	9
3'-(N-methylureido)acetophenone O-(trichloroacetyl)oxime	10 1	5	7	9	3	9	9	9	9	5	7	9	9	9	9	9	9	8	9	9	7	9	9	9	9
3'-(N',N'-dimethylureido)aceto- phenone O-(2,4-trichlorophenoxy- acetyl)oxime	10 1	0	3	0	0	3	8	6	6	4	6	9	9	9	9	9	9	6	9	9	9	9	9	9	9
3'-(N',N'-dimethylureido)aceto- phenone O-(2,4,5-trichlorophenoxy- acetyl)oxime	10 1	0	0	0	0	0	0	0	5	5	4	7	9	9	9	9	9	4	8	8	0	9	9	9	9
3'-(N'-methylureido)acetophenone O-(10-undecenyl)oxime	10 1	5	8	9	4	9	9	9	9	6	6	9	5	9	9	9	9	5	7	9	0	8	9	9	9

Example 9

Fungicidal Activity

5 The fungicidal activity of the compounds of the invention was investigated by one or more of the following tests.

1. Direct activity

10 Intact leaves or leaf pieces of wheat and cucumber were supported on water-saturated seed germination pads in 9 cm petri dishes and were sprayed with aqueous suspensions containing 1000 ppm of the test compound. The leaves or leaf pieces were allowed to dry and were then inoculated with spores of *Puccinia recondita* (brown wheat rust) and
15 *Erysiphe cichoracearum* (cucumber powdery mildew) respectively. Observations on the development of disease symptoms were made after 2—7 days.

2. Systemic activity

A quantity of 12 mg of the finely ground test compound was applied to the surface of each of three soil samples contained in separate 2" X 2" plastic pots. The soil samples were then sown each with 12 wheat seeds which were covered with soil and allowed to grow for 10 days. The resulting plants were then inoculated with spores of *Puccinia recondita* (brown rust) and observations on the development of the fungus were made after 7 days.

The results of the tests are set out in Table 3, in which a result 2 indicates more than 80% control of the fungal disease, a result 1 indicates 50—80% control and a result 0 indicates less than 50% control.

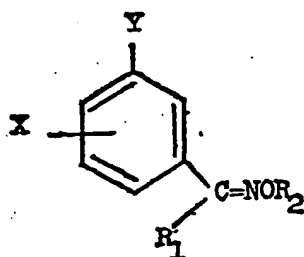
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TABLE 3

	Fungicidal Activity			
	Direct Activity		E. cichoracearum	Systemic Activity
	P. recondita			
3'-isopropoxycarbonylaminoacetophenone oxime	1		2	—
3'-propionamidoacetophenone oxime	1		2	—
3'-(N',N'-dimethylureido)acetophenone oxime	2		2	2
3'-(N',N'-dimethylureido)acetophenone O-methyloxime	—		—	2
3'-(N'-methylureido)acetophenone oxime	2		2	2
3'-(N',N'-dimethylureido)acetophenone O-(4-chloro-2-methylphenoxyacetyl)oxime	2		2	—
3'-(N',N'-dimethylureido)acetophenone O-acetyloxime	2		2	2
3'-(N'-methylureido)acetophenone O-acetyloxime	2		2	2
3'-(N'-methylureido)acetophenone O-octanoyloxime	2		2	2

WHAT WE CLAIM IS:—

1. Phenyl ketoxime derivatives of general formula:—



5 wherein R_1 represents an alkyl group; R_2 represents a hydrogen atom, an alkyl or aralkyl group, a phenyl group substituted by nitro and fluoroalkyl, or an acyl group; X represents a hydrogen or halogen atom or an alkoxy, alkylthio or alkylureido group; and Y represents an amino, ureido or thioureido group optionally substituted by alkyl, phenyl, alkylphenyl or by acyl.

2. Phenyl ketoxime derivatives as claimed in claim 1 wherein R_1 represents an alkyl group of 1—6 carbon atoms; R_2 represents a hydrogen atom, an alkyl group of 1—6 carbon atoms, a benzyl group, a phenyl group substituted by one or two nitro groups and by a fluoroalkyl group of 1—6 carbon atoms, an optionally chloro-substituted alkanoyl group of up to 10 carbon atoms, an alkanoyl group of up to 6 carbon atoms substituted by a phenoxy group bearing chloro or alkyl substituents, an alkenoyl group of up to 12 carbon atoms, a benzyloxycarbonyl group, a chloro-substituted benzoyl group, or a carbamoyl group mono- or di-N-substituted by alkyl of 1—6 carbon atoms; X represents a hydrogen or chlorine atom, or an alkoxy, alkylthio or alkylureido group in which the alkyl group is of 1—6 carbon atoms; and Y represents an amino group substituted by alkyl of 1—6 carbon atoms, by alkanoyl of up to 6 carbon atoms optionally bearing a chloro or chloro-phenoxy substituent, by alkoxy-carbonyl of up to 6 carbon atoms, or by benzyloxycarbonyl, a ureido group optionally substituted by one or two alkyl groups of 1—6 carbon atoms or by a phenyl or tolyl group, or a thioureido group substituted by alkanoyl of up to 6 carbon atoms.

3. Phenyl ketoxime derivatives as claimed in claim 2 wherein R_2 represents a hydrogen atom, an alkyl group of 1—6 carbon atoms or a carbamoyl group mono- or di-N-substituted by alkyl of 1—6 carbon atoms; X represents a hydrogen atom; and Y represents an amino group substituted by optionally chloro-substituted alkanoyl of up to 6 carbon atoms, by an alkoxy-carbonyl group of 1—6 carbon

atoms, or by a benzyloxycarbonyl group, or a ureido group substituted by one or two alkyl groups of 1—6 carbon atoms.

4. Phenyl ketoxime derivatives as claimed in claim 2 wherein R_1 represents a methyl or propyl group; R_2 represents a hydrogen atom or a methyl group, a benzyl group, a phenyl group substituted by one or two nitro groups and by a trifluoromethyl group, an acetyl, trichloroacetyl, octanoyl, dichlorophenoxyacetyl, trichlorophenoxyacetyl or chloro-methylphenoxyacetyl group, an undecenyl group, a benzyloxycarbonyl group, a trichlorobenzoyl group of a N-methyl or N,N-dimethylcarbamoyl group; X represents a hydrogen or chlorine atom or a methoxy, methylthio or methylureido group; and Y represents an amino group substituted by methyl, acetyl, chloroacetyl, propionyl, dichlorophenoxyacetyl, ethoxycarbonyl, isopropoxycarbonyl or by benzyloxycarbonyl, a ureido group substituted by one or two methyl groups or by a phenyl or tolyl group or a thioureido group substituted by acetyl.

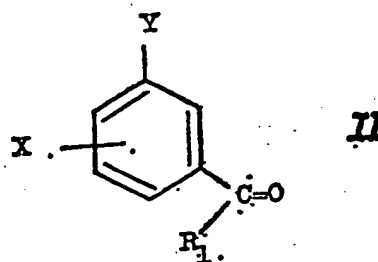
5. 3' - (N' - methylureido) acetophenone oxime.

6. 3' - (N',N' - dimethylureido) acetophenone O-methyloxime.

7. 3' - (N' - methylureido) acetophenone O - (4 - chloro - 2 - methylphenoxyacetyl) oxime.

8. Phenyl ketoxime derivatives as claimed in claim 1 specifically named herein excluding those claimed in claims 5, 6 and 7.

9. Process for preparing phenyl ketoxime derivatives as claimed in claim 1 wherein R_2 represents a hydrogen atom or an alkyl group, which comprises reacting a phenyl ketone of general formula:—



with a hydroxylamine derivative of formula:—



III

or an acid salt thereof.

10. Process for preparing phenyl ketoxime derivatives as claimed in claim 1 wherein R_2 represents an aralkyl or acyl group or a phenyl group substituted by nitro or fluoroalkyl, which comprises reacting the corresponding compound wherein R_2 represents a hydrogen atom

with a base and a halo compound of formula:—



IV

5 wherein Hal represents a halogen atom, or, when R_2 represents an N-alkyl-substituted carbamoyl group, with an alkyl isocyanate.

11. Process according to claim 9 or 10 substantially as hereinbefore described.

10 12. Process according to claim 9 or 10 substantially as described in examples 1—6.

13. Phenyl ketoxime derivatives as claimed in claim 1 when prepared by a process according to any one of the claims 9—12.

14. Pesticidal compositions comprising a

15 carrier or a surface-active agent or both a carrier and a surface-active agent, together with an active ingredient, at least one phenyl ketoxime derivative as claimed in any one of the claims 1—8 or 13.

20 15. Method of combating unwanted plant growth and/or fungi at a locus which comprises applying to the locus a phenyl ketoxime derivative as claimed in any one of the claims 1—8 or 13 or a composition as claimed in claim 14.

25

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